

RECOVERY AND UTILIZATION OF FLY ASH CARBONS FOR THE DEVELOPMENT OF HIGH-VALUE PRODUCTS

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The implementation of increasingly stringent Clean Air Act Regulations by the coal utility industry has generally resulted in an increase in the concentration of unburned carbon in coal fly ash due to the installation of low-NO_x burners. Although nowadays the fate of the unburned carbon is mainly disposal, this carbonaceous material is a very attractive precursor for the production of premium carbon products, since it contains >99% carbon and it has gone through a devolatilization process while in the combustor at temperatures well above 1300°C. Accordingly, this work has investigated two potential routes for the generation of premium carbon products from the unburned carbon present in fly ash. The first route focuses on the use of fly ash carbons as precursors for activated carbons by steam activation at 850°C, while the second route concentrates on the utilization of fly ash carbons as a replacement for calcined petroleum coke in the production of carbon artifacts.

INTRODUCTION

The implementation of increasingly stringent Clean Air Act Regulations by the coal utility industry has resulted in an increase in the concentration of unburned carbon in coal combustion fly ash. In 1998, around 5-8 million tons of unburned carbon were disposed, due to the present lack of efficient routes for its utilization. However, the increasingly severe regulations on landfill and the limited access to new disposal sites with the subsequent rise in the cost of disposal, may demand the utility industry to begin offsetting coal combustion with natural gas, or require additional coal cleaning to remove the ash prior to combustion, or simply start utilizing the unburned carbon. The authors have previously conducted extensive studies on the characterization of unburned carbon and showed that its properties are similar to those of conventional precursors for the production of premium carbon materials [1, 2]. Accordingly, this research program focuses on the development of routes for the generation of premium carbon products from the unburned carbon present in fly ash.

The utilization of fly ash carbons can bring enormous economical and environmental benefits to both the coal and utility industries. Although several technologies have been successfully developed to separate the unburned carbon from the fly ash, only a few power plants have installed a beneficiation process on their sites. This is due to the low value of the resultant separated materials, since a ton of fly ash is generally sold for as little as \$10-20, and the unburned carbon is simply disposed or re-routed to the combustor. However, the economics of this process can be greatly enhanced if both separated materials can be used as precursors for value-added products. In fact, this is the case for the unburned carbon, which can be used as an excellent precursor for the generation of premium carbon products, like activated carbons and carbon artifacts. Therefore, the added value generated from the fly ash carbon utilization would clearly offset the cost of the separation process. For instance, the average price for a ton of activated carbon ranges from \$500 up to \$4000, which implies a potential 25-200 fold increase compared to the price of the ash (<\$ 20/tonne). For the case of carbon artifacts, the calcined petroleum coke used for their manufacture usually costs ~ \$ 220-250 / ton.

EXPERIMENTAL

Procurement of fly ash samples The fly ashes were collected from Portland station Unit #2 (Northampton County, PA) with a net capacity of 243 MW and operated by GPU Genco. Samples were collected all the way from the economizer through the hoppers to the stack, amounting to a total of 16 samples. The hoppers were emptied prior to collection in order to obtain fresh ash. The carbon contents of the fly ashes were determined according to the ASTM C311 procedure and the fly ash with the highest carbon concentration was chosen as feedstock for the production of the carbon products.

Activation of fly ash carbons The activation of the samples was carried out in an activation furnace, that consists of a stainless steel tube reactor inside a vertical tube furnace, as previously described [3]. Typically 3 g of sample was held isothermally at 850°C for periods of 60 minutes in flowing steam. The porosity of the samples was characterized conducting N_2 adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASiT. The BET surface areas were calculated using the adsorption points at the relative pressures (P/P_0) 0.05 - 0.25. The total pore volume, V_{TOT} , was calculated from the amount of vapor adsorbed at the relative pressure of 0.95. The mesopore (pores 2-50 nm in width) and micropore (pores <2 nm in width) volumes were calculated using the BJH and DR equation, respectively.

Manufacture of carbon artifacts The fly ashes with the highest carbon levels (40-50 wt%) were chosen as feedstocks for the beneficiation step conducted prior to the manufacture of carbon pellets. The beneficiation protocol was performed to be able to elucidate the interactions between the unburned carbon and the pitch, that otherwise may be masked by the high ash concentrations, and included first a flotation separation followed by an acid digestion step using a HF/HCl solution to reduce the inorganic content to ~3 wt%. The carbon pellets were produced from mixtures of this concentrated fly ash carbon (CFAC), a petroleum coke (PC) and a coal tar binder pitch (CTBP). The mixtures were heated to ~130°C and pressed into pellets. The absolute densities of the precursors and the pellets were measured by using a Quantachrome MVP-1 Multi Pycnometer with helium as density medium.

RESULTS AND DISCUSSION

Carbon variations between hoppers Fly ash samples were collected from each of the hoppers and Figure 1 shows the configuration and gas flow for the hoppers, and the carbon values of the corresponding fly ashes. The hot-side bins (1-2) present LOI contents of only 10-12%, that become higher for hoppers 5-6 (15 and 19%, respectively) and 9-10 (32 and 36%, respectively) and reach a maximum for the cool-side hoppers 13 and 14 (36 and 50%, respectively). Although this trend also prevails for the train of hoppers 3-7-11-15, it is not so clear, since the LOI values vary only between 14-18%. This "hot-side" and "cool-side" terminology has been adopted from former studies and it is based on characteristics of the respective ashes, where fly ashes from hot-side collectors present characteristics associated with higher temperatures (lower carbon content and larger fly ash sizes) compared to those of their cool-side counterparts [4].

Activation of fly ash carbons Figure 2 shows the N_2 -77K adsorption isotherms for three fly ash carbon samples, designated as FAC-A, FAC-B and FAC-C, and illustrates the inherent porosity of these materials. All the adsorption isotherms are Type II according to the BDDT classification and they are typical for nonporous or macroporous adsorbents, on which unrestricted monolayer-multilayer adsorption can occur [2].

Table 1 lists the BET surface areas (SA) and total pore volume (V_{TOT}) for the precursors. The three samples have surface areas between 30-40 m^2/g . Previous studies conducted by the authors on a range of fly ashes and Density Gradient Centrifugation concentrates have shown that the extensive and rapid devolatilization that coal undergoes in the combustor, seems to promote the generation of meso- and macropores [2]. Pore size distribution studies were also conducted and showed that the pore volume is mainly due to mesopores, with the mesopore volume accounting for over 60% of the total pore volume [2]. The solid yields of the three FAC samples activated for 60 minutes are also listed in Table 1. Despite the low particle size of the FAC samples, the solid yields are relatively high, since the FAC has already undergone devolatilization in the combustor. This makes the UC an attractive precursor for the production of activated carbons, since they present much higher solid yields than conventional precursors, such as wood. FAC-A presents higher solid yields than FAC-B (73% vs. 55%), due to their larger particle size (200 μm vs. 45 μm). Previous studies have shown that the particle size of the precursor strongly affects the solid yields of the resultant activated samples, with higher yields for bigger particle size fractions [5].

Figure 3 shows the N_2 -77K adsorption isotherms for the three steam activated FAC samples. Although the isotherms now look more like Type I, concave to the P/P_0 axis, that are typical for microporous materials, they do not reach a plateau at high relative pressures, indicating the presence of some meso- and macro-porosity. The activated carbons generated from the samples FAC-A and FAC-B present higher adsorption isotherms than that of FAC-C. This is reflected in FAC-A-Act and FAC-B-Act exhibiting surface areas and pore volumes higher than that of FAC-C-Act (332 and 443 m^2/g vs 110 m^2/g , Table 1). This may be due to the lower steam flowrates used for the first two samples, resulting in more favorable conditions for the production of activated carbons. The higher ash content of FAC-C compared to that of FAC-A and FAC-B may also play a detrimental role in the activation of this sample. Further activation studies are being conducted to ascertain the role of the ash in the activation process of the unburned carbon.

Figure 4 compares the meso- and micropore volume for the precursors and the activated samples. As previously described, the inherent porosity of the UC samples is highly mesoporous, with the

mesopore volume accounting for ~ 66% of the total pore volume. The activation process promotes the development of micropores, with the micropore volume now accounting for over 60% of the total. Pore size distribution studies and CO₂ porosity measurements are in progress.

Properties of carbon pellets prepared with fly ash carbons In the preparation of conventional carbon materials, the petroleum coke is used as filler and it is normally separated into at least three different particle size fractions: fine (<200 mesh); intermediate; and coarse (>20 mesh), to obtain improved packing densities. Due to the nature of the combustion process, most fly ashes are milled to the size of the fine fraction or less used for the production of carbon materials. Hence, this study concentrated on the production of carbon pellets, where the fine fraction of petroleum coke was replaced by unburned carbon. Table 2 lists the absolute densities for the carbon pellets produced with the concentrate of fly ash carbon (CFAC), the conventional calcined petroleum coke (PC) and coal tar binder pitch (CTBP). As expected, the density of the carbon pellet A, consisting of 20 wt% coal tar binder pitch and 80 wt% petroleum coke, is slightly lower than that of the petroleum coke itself (1.76 g cm⁻³ vs. 1.89 g cm⁻³). This is due to the lower density of the CTBP (1.25 g cm⁻³), and can be derived from direct calculation of the two fractions (0.2*1.25 g cm⁻³ + 0.8*1.89 g cm⁻³ = 1.76 g cm⁻³). Therefore, for conventional carbon pellets, the CTBP seems to mostly be filling the vacant voids between the PC particles. For pellet B, where all the fine fraction of petroleum coke has been replaced by concentrate unburned carbon, there was a difference between the observed and calculated densities (1.76 g cm⁻³ vs. 1.65 g cm⁻³). This indicates that there is a synergistic filling effect between the unburned carbon and the coal tar binder pitch, that is reflected in a densification of the carbon pellets produced. This could presumably be related to the higher surface area of the concentrated unburned carbon of ~50 m²/g compared to that of 5 m²/g for the calcined petroleum coke, and we are presently conducting further studies to characterize this interaction. These results are very encouraging for further baking of the pellets into artifacts, that is now underway in our laboratory.

CONCLUSIONS

The present work has investigated novel routes for the use of unburned carbon as a high value product. The detailed study of a series of fly ash hoppers has revealed that cool-side bins present the highest LOI values (50%) and therefore they could be suitable hoppers for the collection of high carbon content ashes as precursors for carbon materials. This work has demonstrated the ability of unburned carbon from coal combustion waste to generate activated carbons by steam activation, where after 60 minutes activation time, the unburned carbon samples generated activated carbons with microporous structure and surface areas up to 443 m²/g. Despite the low particle size of the samples investigated, the solid yields are relatively high, since the unburned carbon has already gone through a devolatilization process in the combustor. The activation process can tailor the inherent mesoporosity of these materials into the desired porosity for a specific application. For the case of the carbon artifacts, although the fly ash carbon presents lower density than petroleum coke, the density of the carbon pellets prepared with unburned carbon is comparable to that using only petroleum coke, probably due to a strong interaction between the unburned carbon and the coal tar binder pitch.

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Table 1. Solid yield, BET surface area and total pore volume for the fly ash carbon samples and their activated counterparts.^a

Sample	Activation time / min	Solid yield / % weight	BET S.A. / m ² /g	V _{total} / cc/g
FAC-A	--	--	40	0.03
FAC-B	--	--	38	0.03
FAC-C	--	--	30	0.02
FAC-A-Act	60	73	332	0.15
FAC-B-Act	60	55	443	0.14
FAC-C-Act	60	79	110	0.04

^a The solid yields and surface areas are expressed in ash free basis.

Table 2. Absolute densities of the carbon pellets prepared.

Pellet	Composition	Density / g cm ⁻³	
A	20% CTBP, 40% intermediate CFAC, 40% fine PC	1.76 ^a	1.76 ^b
B	20% CTBP, 40% intermediate CFAC, 40% fine UC	1.76 ^a	1.65 ^b

^a Density measured by helium pycnometry.

^b Calculated density.

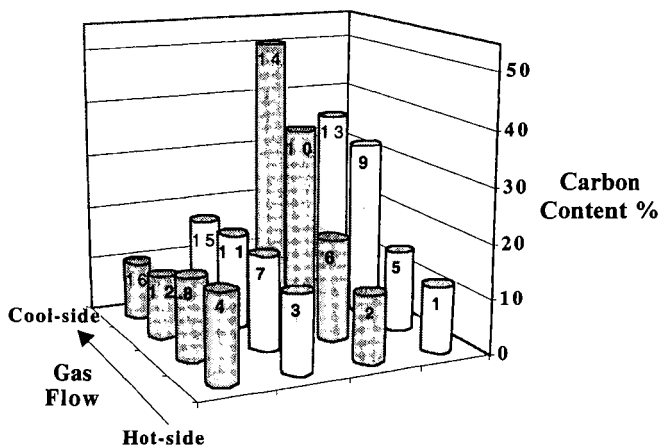


Figure 1. Variation in carbon contents of the fly ashes collected from the different hoppers. The numbers on the bars indicate hopper no.

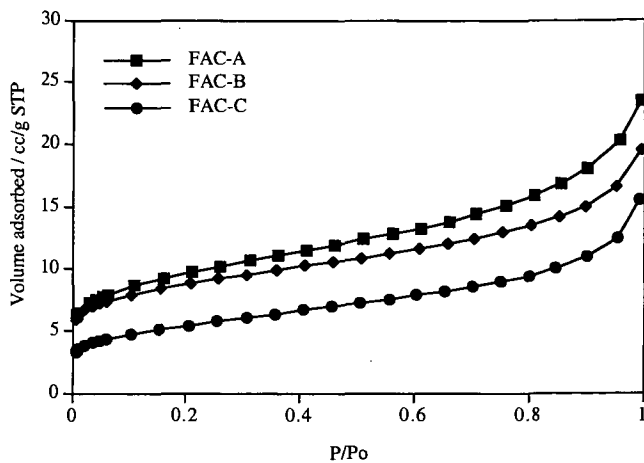


Figure 2. N_2 -77K adsorption isotherms for the fly ash carbons.

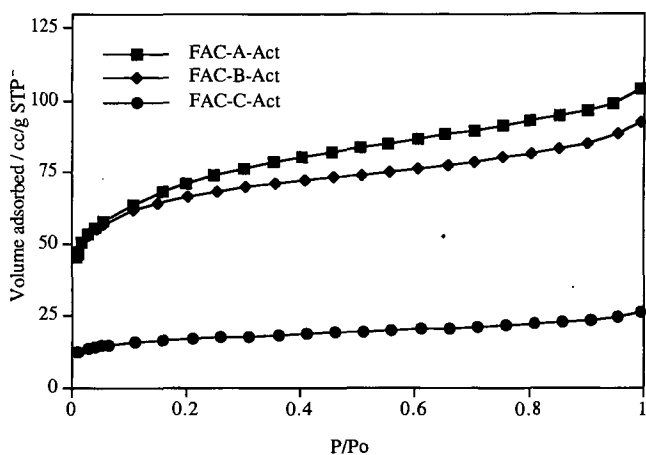


Figure 3. N_2 -77K adsorption isotherms for the activated samples.

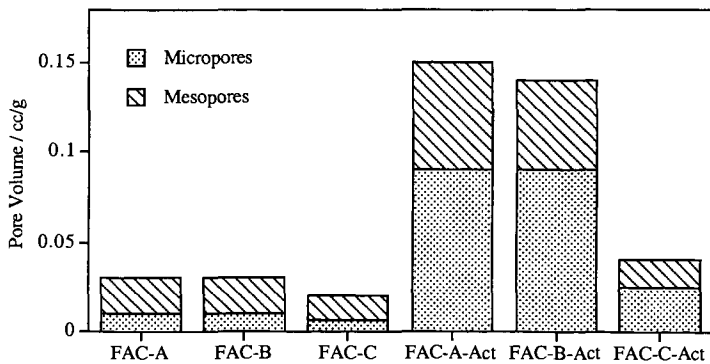


Figure 4. Distribution of the micro- and mesopore volume of the FACs and their activated samples.